Theor Chim Acta (1990) 78: 1–9

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Chimica Acta

Isomorphic electron orbitals for vibronic flexibility in a cyclopropenyl radical molecular device

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Received January 3, 1990; received in revised form May 7, 1990/Accepted May 23, 1990

Summary. The vibronic character of this molecular device has been studied using isomorphic electron orbitals. The leading role of the softest vibrational mode for the electron transport process is stressed by the quantum mechanical treatment of the rearrangement operator. The theory was used to investigate the possible function of the soliton valve, which has been suggested as a switching tip. The electronic flexibility of the cyclopropenyl radical with respect to molecular vibrations, which is important for the function of the molecular device, is well characterized by the hardness and softness of the electron structure in terms of the orbital energy-occupation number correlation diagram.

Key words: Isomorphic orbital – Vibronic electron transport – Molecular device

1. Introduction

Recently, Carter has suggested the intrinsic importance of molecular tips in future electronic devices [1–3]. Since then many models of molecular devices have been proposed. In this connection, theoretical analysis of the response properties of molecular electronic structure to internal and external perturbations, e.g. molecular vibration and an electromagnetic field, has become of vital importance [4]. In particular, the microscopic vibronic interaction should play an important role in electron transferability in the molecular aggregates [5]. Consequently, it is interesting to investigate the vibronic structure on the basis of the molecular orbital method [6].

We have proposed a method, called the isomorphic orbitals [8, 9], which generalizes the Amos–Hall corresponding orbital method [7] for vibronic electron orbitals. We have formulated the rearrangement operator in the role of an evolution operation [10] for the isomorphic electron orbitals. The rearrangement operator has some relationship with the nonadiabatic coupling operator for the dynamic Fock equation [11].

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In this paper, we will analyze the vibronic flexibility of cyclopropenyl radical which may be used as a unit of the soliton valve in a switching tip of a molecular device [12]. The facility or difficulty of the electron transport accompanying the molecular vibration is examined by utilizing isomorphic electron orbitals [8]. This has a theoretical connection with the Kohn anomaly in the field of condensed matter physics [13].

2. Isomorphic electron orbitals

Isomorphic electron orbitals are given by rearranging natural orbitals [14] $\{\psi_m(0)\}$ and $\{\psi_j(1)\}$ at two adjacent points s_0 and s_1 of the intrinsic reaction coordinate (IRC) [15, 16] in such a way that the overlap matrix among them becomes diagonal:

$$\langle\tilde{\psi}_k(0)|\tilde{\psi}_n(0)\rangle = \delta_{kn}, \tag{1a}$$

$$\langle\tilde{\psi}_k(1)|\tilde{\psi}_n(1)\rangle = \delta_{kn}, \tag{1b}$$

$$\langle\tilde{\psi}_k(0)|\tilde{\psi}_n(1)\rangle = \sqrt{\gamma_k}\,\delta_{kn}. \tag{1c}$$

If we take the limit $s_1 \to s_0$, so that $\{\tilde{\psi}_k(1)\} \to \{\tilde{\psi}_k(0)\}$, and after that let s_0 be varied as we move along the reaction coordinate, then we can get the isomorphic electron orbitals $\{\tilde{\psi}_k\}$ which represent the smooth electron current accompanying a chemical reaction. The occupation numbers $\{\tilde{\nu}_k\}$ of the electron orbitals $\{\tilde{\psi}_k\}$ are defined [8, 9] as the expectation values of the first order density matrix ρ [14]. Similarly the orbital energies $\{\tilde{\varepsilon}_k\}$ of the electron orbitals $\{\tilde{\psi}_k\}$ are defined [9] as the expectation values of the natural orbital Hamiltonian operator [17], or Fock operator within the Hartree–Fock approximation.

The isomorphic electron orbitals $\tilde{\psi}_k(0)$ and $\tilde{\psi}_k(1)$ are represented as follows:

$$\tilde{\psi}_k(1) = \sum_i U_{ik}\psi_i(1), \tag{2a}$$

$$\tilde{\psi}_k(0) = (1/\sqrt{\gamma_k}) \sum_j \sum_m S_{mj} U_{jk} \psi_m(0). \tag{2b}$$

In these formulas, S_{mj} denotes the overlap integral and U_{ik} and γ_k denote the eigenvector and eigenvalue of the rearrangement operator $\|R_{ij}\|$ constructed from S_{mj}, respectively:

$$S_{mj} = \langle\psi_m(0)|\psi_j(1)\rangle, \tag{3}$$

$$\sum_j R_{ij} U_{jk} = U_{ik}\gamma_k, \tag{4a}$$

$$\sum_i U^*_{ik} U_{in} = \delta_{kn}, \tag{4b}$$

where

$$R_{ij} = \sum_m S^*_{mi} S_{mj}, \tag{5a}$$

$$R_{ij} = R^*_{ji}. \tag{5b}$$

Let the two points s_0 and s_1 be very close to each other. Then the Taylor series expansion of R_{ij} in terms of $\Delta s = s_1 - s_0$ is given as follows:

$$R_{ij} = R^{(0)}_{ij} + R^{(1)}_{ij}\,\Delta s + R^{(2)}_{ij}\,\Delta s^2 + o(\Delta s^3). \tag{6a}$$

$$R_{ij}^{(0)} = \delta_{ij}, \tag{6b}$$

$$R_{ij}^{(1)} = 0, \tag{6c}$$

$$R_{ij}^{(2)} = -\langle \partial\psi_i/\partial s|\partial\psi_j/\partial s\rangle + \sum_m \langle \partial\psi_i/\partial s|\psi_m\rangle\langle\psi_m|\partial\psi_j/\partial s\rangle. \tag{6d}$$

If we substitute Eq. (6) into Eq. (4a), we have

$$\sum_j (\delta_{ij} + R_{ij}^{(2)}\,\Delta s^2)U_{jk} = U_{ik}\gamma_k. \tag{7}$$

Then we observe that R_{ij} becomes equivalent to $R_{ij}^{(2)}$, which satisfies

$$\sum_j R_{ij}^{(2)} U_{jk} = U_{ik}\,\gamma_k^{(2)}, \tag{8}$$

and that the γ_k is given as

$$\gamma_k = 1 + \gamma_k^{(2)}\,\Delta s^2. \tag{9}$$

In quantum mechanical treatments of nuclear vibration, each order of the nuclear fluctuation is estimated by the non-zero finite value. The general expression of the rearrangement operator may then be defined as follows:

$$\bar{R}_{ij} = \langle R_{ij}\rangle_{\text{av.}}, \tag{10}$$

where $\langle\rangle_{\text{av.}}$ denotes the average with respect to the quantum mechanical nuclear vibration. Of course the nuclear vibration is not limited to the direction of the reaction coordinate, and hence the fluctuation is not limited to a point on the reaction pathway. This rearrangement operator is Hermitian and has the following eigenvalues and eigenvectors:

$$\sum_j \bar{R}_{ij}\bar{U}_{jk} = \bar{U}_{ik}\bar{\gamma}_k, \tag{11a}$$

$$\sum_i \bar{U}_{ik}^{*}\bar{U}_{in} = \delta_{kn}, \tag{11b}$$

which are the counterparts of Eqs. (4a) and (4b). The isomorphic electron orbitals are given as follows:

$$\bar{\psi}_k(1) = \sum_i \bar{U}_{ik}\psi_i(1), \tag{12a}$$

$$\bar{\psi}_k(0) = (1/\sqrt{\bar{\gamma}_k}) \sum_j \sum_m S_{mj}\bar{U}_{jk}\psi_m(0), \tag{12b}$$

which are the counterparts of Eqs. (2a) and (2b). In this case, we obtain the following orthonormal relations:

$$\langle\langle \bar{\psi}_k(0)|\bar{\psi}_n(0)\rangle\rangle_{\text{av.}} = \delta_{kn}, \tag{13a}$$

$$\langle\langle \bar{\psi}_k(1)|\bar{\psi}_n(1)\rangle\rangle_{\text{av.}} = \delta_{kn}, \tag{13b}$$

$$\langle\langle \bar{\psi}_k(0)|\bar{\psi}_n(1)\rangle\rangle_{\text{av.}} = \sqrt{\bar{\gamma}_k}\,\delta_{kn}, \tag{13c}$$

which are the counterparts of Eqs. (1a)–(1c). Occupation numbers and orbital energies are similarly introduced.

It should be noted that if we consider only the zero-point vibrations at a stable equilibrium point, then the leading term of $\bar{R}_{ij}$ in Eq. (10) is given by the contribution of the motion along the IRC:

$$\bar{R}_{ij} \sim R_{ij}^{(0)} + \{1/(2\omega_{\text{min}})\}R_{ij}^{(2)}, \tag{14a}$$

$$\bar{\gamma}_k = 1 + \{1/(2\omega_{\text{min}})\}\gamma_k^{(2)}, \tag{14b}$$

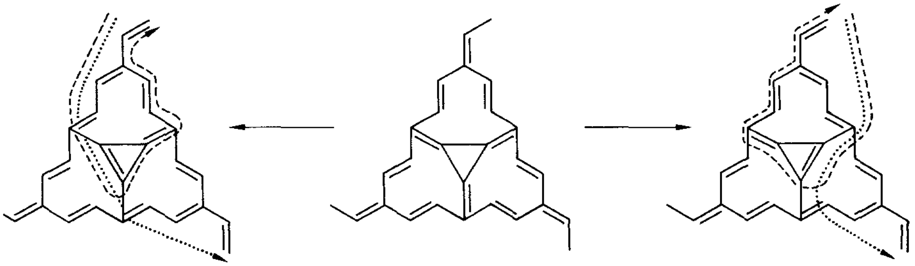
where $\omega_{\min}$ denotes the minimum vibrational frequency of the system at the stable equilibrium point, and where we have used the result that the IRC converges to the normal mode of the minimum force constant, namely the *softest* vibrational mode, by virtue of the stable limit theorem [16(b)]. This shows that electron rearrangement along the IRC plays a leading role at the absolute zero temperature in the quantum mechanical treatment.

3. Electronic flexibility of the soliton valve

Figure 1 shows the soliton valve which Carter has suggested as a molecular switching tip [12]. The soliton valve contains a cyclopropenyl radical fragment as a valve unit. The soliton passage is mediated through the dimerized ethylenic or allylic structure of cyclopropenyl radical. Note that the action of the valve is not as simple as Fig. 1 suggests. This is because there is another reaction channel in the 2 and 2′ states of the valve in addition to the soliton passage channel (depicted by the dotted line in Fig. 1), and the total reflection channel (depicted by the broken line in Fig. 1), namely an isomeric reaction channel between the ethylenic and allylic structures of the cyclopropenyl radical valve unit. The existence of the isomerization channel was reported by the ESR experiment [18]. We shall discuss the electronic flexibility for the isomerization reaction channel of the cyclopropenyl radical to clarify this problem.

3.1. Reaction coordinate

An equilateral cyclopropenyl radical undergoes Jahn–Teller distortion and may transform to two lower-symmetry structures: ethylenic and allylic forms [19, 20]. The MCSCF/3-21G calculation of Chipman et al. [20(a)] indicates that the C_s symmetry forms are more stable than the C_{2v} symmetry forms, and the ethylenic form is a local minimum while the allylic form is a transition state for pseudorotation. The C_s symmetry allylic form has the single A'' CH bending vibrational mode with an imaginary frequency which leads to the equilibrium C_s symmetry ethylenic form. Three local minima and transition states are found in a period of the pseudorotation.



2 1 2′

Fig. 1. Plausible operation of soliton valve. The soliton passage channel is depicted by the *dotted line*, and the reflection channel by the *broken line*

We are interested in the planar forms of the soliton valve. Both the planar ethylenic and allylic forms are unstable with respect to the out-of-plane motions of the hydrogen atoms, though they can be regarded as the equilibrium forms with respect to in-plane vibrational motions [20(a)]. Then we have six local minima with respect to the in-plane pseudorotation coordinate. We adopted the restricted pseudorotation coordinate for the equilateral triangle [21, 22] instead of the steepest descent reaction coordinate [15], and have used the UHF/4-31G wavefunction [23, 24]. The quality of the wavefunction is sufficient to discuss the response property of electrons against the molecular vibration, which is the object of our interest; this is because the response property is so universal as to allow one to neglect electron-electron interactions, as occurs, for example, in the theory of the Kohn anomaly and related subjects [13]. The GAUSSIAN80 [25] and GAUSSIAN82 [26] programs and requisite subroutines are used in this study.

The optimized C_{2v} structures are depicted in Fig. 2. These structures are not stable with respect to the out-of-plane motion. Normal vibrational frequencies and their symmetry assignments are summarized in Table 1. We shall use the two in-plane normal modes of a_1 and b_2 symmetries to define the restricted pseudo-rotation coordinate [22]. These modes correspond to the minimum frequencies in the plane, which play a central role in the electron rearrangement process, as shown in Sect. 2.

The pseudorotation coordinate is defined by

$$\delta x_\alpha = v_{a_1,\alpha}\varrho \cos\theta + v_{b_2,\alpha}\varrho \sin\theta, \tag{15}$$

where $v_{a_1,\alpha}$ and $v_{b_2,\alpha}$ are the normal vibrational mode vector of αth nucleus with a_1 and b_2 symmetries, respectively. The radius and the center of the circle are determined so as to make the carbon skeleton of the molecule form an equilateral triangle, when the molecule distorts along the normal vibrational mode of a_1 symmetry. Then the reaction coordinate is θ. The center and the radius are different for each ethylenic and allylic structures. A schematic representation of the reaction coordinate (depicted by the solid line), the cell structure [16(b)] of the potential energy surface (depicted by the broken line) and

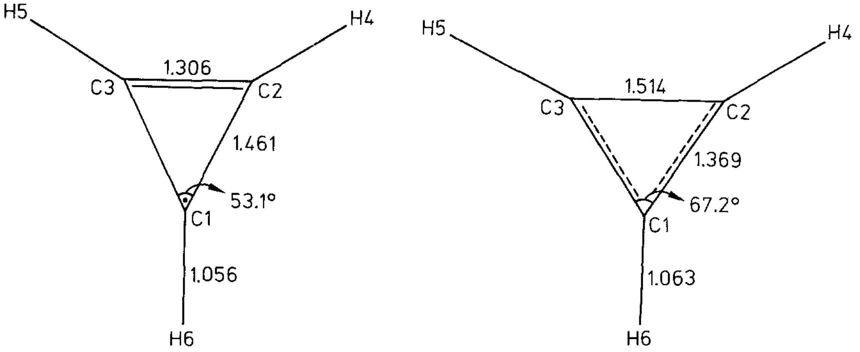


Fig. 2. Optimized geometries of the planar ethylenic and allylic structures of the cyclopropenyl radical. C_{2v} symmetry is assumed (in Å and degree)

Table 1. Harmonic vibrational frequencies (cm^{-1}) for the C_{2v} in-plane ethylenic and allylic structure of the cyclopropenyl radical

Ethylenic		Allylic	
b_2	970.0	b_2	847.0
a_1	1033.7	a_1	902.7
b_2	1111.4	b_2	1062.7
a_1	1303.4	a_1	1129.9
b_2	1495.0	b_2	1255.9
a_1	1770.0	a_1	1562.0
b_2	3502.9	a_1	3453.7
a_1	3521.9	b_2	3524.4
a_1	3568.0	a_1	3559.4
out-of-plane mode[a]		out-of-plane mode[a]	
b_1	1039.1i	a_2	672.9i
b_1	707.9	b_1	577.3i
a_2	991.7	b_1	922.9

[a] i denotes imaginary frequency

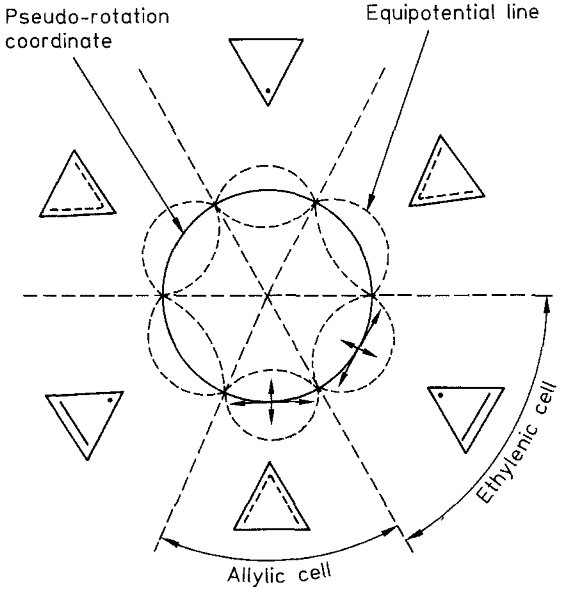


Fig. 3. Pseudorotation reaction coordinate, cell structure and equi-potential line

the equi-potential line (depicted by the dotted line) are shown in Fig. 3. The cell structure [16(b)], which is constructed from the neighboring domain of the stationary point of the potential energy surface, is important because it imposes the boundary condition on the nuclear wavefunction. An elucidation of the cell structure from the electronic structural point of view is interesting in the light of flexibility of the electronic structure.

3.2. Response property of the cell structure

Canonical SOMO (singly occupied molecular orbital) and LUMO orbitals are drawn schematically in Fig. 4. The isomerization between the allylic and ethylenic structures must go through a SOMO-LUMO crossing. The correlation diagrams between the orbital energy $\{\tilde{\varepsilon}_k\}$ and the occupation number $\{\tilde{\nu}_k\}$ are calculated. The space of rearrangement operator, i.e. the running range of the suffix of the matrix, is limited in the three π orbitals, one of which is doubly occupied, the second being singly occupied, while the third is virtual within the UHF scheme. We have evaluated Eqs. (6) and (7) numerically using $\Delta s = 10^{-3}\,(\mathrm{amu})^{1/2}$bohr. The rearrangements of the orbital occupation numbers are very small in the ethylenic cell, as is shown in Fig. 5(a). On the contrary, as shown in Fig. 5(b),

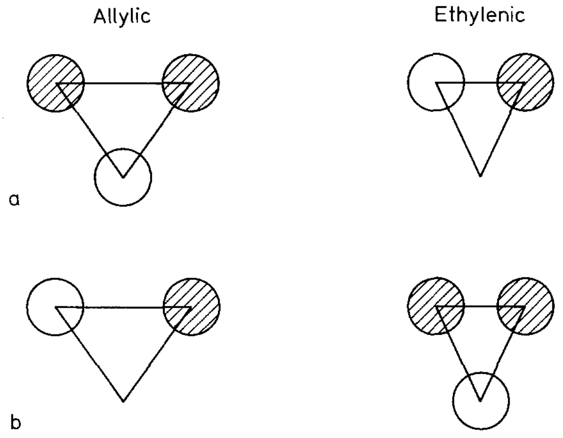


Fig. 4. **a** LUMO, **b** SOMO patterns

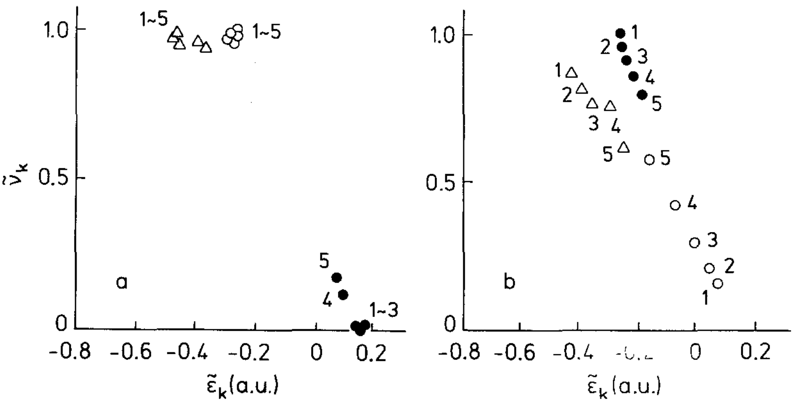


Fig. 5. Energy-occupation number correlation diagram of UHF α-spin electron orbitals for **a** ethylenic and **b** allylic structures of the cyclopropenyl radical. $\tilde{\psi}_1$ (○) denotes LUMO (SOMO) pattern of the allylic (ethylenic) structure, $\tilde{\psi}_2$ (●) denotes SOMO (LUMO) pattern of the allylic (ethylenic) structure, and $\tilde{\psi}_3$ (△) denotes the orbital which has a totally symmetric pattern. The changes are traced along the pseudorotation reaction coordinate θ, and the numbers 1, 2, 3, 4 and 5 indicate that θ is 5°, 10°, 15°, 20° and 25°, respectively

the occupation number of $\tilde{\psi}_1$, which has a LUMO orbital pattern of allylic cyclopropenyl radical from $\theta = 5°$ to $\theta = 25°$, increases in the allylic cell. The electrons are transported from the orbitals $\tilde{\psi}_2$ and $\tilde{\psi}_3$ to the orbital ψ_1, and this characterizes the initial electronic process of the isomerization reaction from the allylic structure to the ethylenic structure. It can be said that the response of the electronic structure to the molecular vibration is small and hence the electronic structure is *hard* in the ethylenic cell. On the other hand, the response is large and the electronic structure is soft in the allylic cell. Moreover the ethylenic cell can be said to be larger than the allylic cell judging from the response property of the electronic structure. The small size of the allylic cell with respect to in-plane distortion is in agreement with the fact that the C_s symmetry allylic form is the transition state for the unconstrained potential surface for the pseudorotation.

4. Concluding remarks

We have applied isomorphic electron orbitals to the problem of the molecular design of a soliton valve. The leading role of the softest vibrational mode for the electron transport process is stressed by the quantum mechanical treatment of the rearrangement operator for the isomorphic electron orbitals. The electronic flexibility of the cyclopropenyl radical against molecular vibrations, which is important for the function of the molecular device, is well characterized by the hardness and softness of the electron structure in terms of the orbital energy-occupation number correlation diagram. It is concluded that the isomorphic electron orbitals provide a good starting point for the molecular design of the vibronic systems.

Acknowledgments. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan, for which the authors express their gratitude. We are also grateful to Data Processing Center of Kyoto University and the Computer Center of the Institute for Molecular Science, for their generous permission to use FACOM M780, VP-400E and HITAC M680-H, S-820 computers, respectively.

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